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PATENT SPECIFICATION

1,015,054

DRAWINGS ATTACHED

1,015,054

Inventor: ERIC CATTERALL.

Date of filing Complete Specification: Jan. 14, 1963.
Application Date: Jan. 1, 1962. No. 3579/62.
(Patent of Addition to No. 880998 dated July 14, 1958).
Complete Specification Published: Dec. 31, 1965.
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Index at acceptance:—C3 P(13D1A, 13D1B, 13D2A, 13D2B, 13D2C, 13F3, 13G4B, 13G6, 13H3, 13N3, 13N4, 13R1, 13R2B)

Int. Cl.:—C 08 d, f

COMPLETE SPECIFICATION

Polymerization of Unsaturated Aliphatic Compounds

ERRATUM

SPECIFICATION No. 1,015,054
Amendment No. 1

Page 1, Heading, Application date, *for* "Jan. 1, 1962." *read* "Jan. 31, 1962."

THE PATENT OFFICE
13th May 1966

the A sub-groups of IV to VII of the Periodic Table with an addition compound of an aluminium alkyl with an ether hereinafter termed "an etherate" and contacting the said aliphatic compound with the said catalyst in the substantial absence of a preformed polymer.

According to the present invention, a process for the polymerization of an unsaturated aliphatic compound containing a $CH_2{=}\overset{|}{C}-$ group comprises forming a heterogeneous surface-active catalyst by mixing together a vanadium compound and an addition compound of an aluminium alkyl with diisopropyl ether and contacting the aliphatic compound with the said catalyst.

Heterogeneous surface-active catalysts are of the type whereby the polymerization is effected by the absorption of the monomer on the active surface thereof.

The addition compound of an aluminium alkyl and diisopropyl ether referred to above, is prepared by simply mixing at room tem-

are the chlorides, for example vanadium trichloride and the oxychlorides. Mixtures of vanadium trichloride and vanadium oxytrichloride can be used, if desired.

The preferred aluminium alkyls are those having the formula AlR_3 wherein Al represents aluminium, and R represents an alkyl group containing up to 8 carbon atoms, for example isobutyl, ethyl, isopropyl or octyl.

The proportion of the addition compound used is preferably from 0.5 to 3 per cent based on the total weight of the monomer and the surface-active catalyst.

Generally, an amount of up to 10 moles of aluminium alkyl per mole of vanadium compound can be employed, but usually the amount is at least 1.5 moles.

If desired, the surface-active catalyst can be absorbed on cryolite or on another finely-divided filler, for example silica or carbon black. The silica can consist of either a three-dimensional cross-linked network, or a lattice distorted by the presence of an element of

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Int. Cl.:—C 08 d, f

COMPLETE SPECIFICATION

Polymerization of Unsaturated Aliphatic Compounds

We, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1, Albany Street, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the polymerization of unsaturated aliphatic compounds, and more particularly compounds containing a $CH_2=\underset{|}{C}$— group and is an improvement in or modification of the invention described and claimed in our Patent Specification No. 880,998.

In our Patent Specification No. 880,998, we have described and claimed a process for the polymerization of an unsaturated aliphatic compound containing a $CH_2=\underset{|}{C}$— group which comprises forming a heterogeneous surface-active catalyst by mixing together a compound of a metal of Group VIII or of the A sub-groups of IV to VII of the Periodic Table with an addition compound of an aluminium alkyl with an ether hereinafter termed "an etherate" and contacting the said aliphatic compound with the said catalyst in the substantial absence of a preformed polymer.

According to the present invention, a process for the polymerization of an unsaturated aliphatic compound containing a $CH_2=\underset{|}{C}$— group comprises forming a heterogeneous surface-active catalyst by mixing together a vanadium compound and an addition compound of an aluminium alkyl with diisopropyl ether and contacting the aliphatic compound with the said catalyst.

Heterogeneous surface-active catalysts are of the type whereby the polymerization is effected by the absorption of the monomer on the active surface thereof.

The addition compound of an aluminium alkyl and diisopropyl ether referred to above, is prepared by simply mixing at room temperature an aluminium alkyl with diisopropyl ether. Alternatively, the addition compound can be prepared by mixing the aluminium alkyl with the ether prior to addition of the vanadium compound, or *in situ* after mixing the aluminium alkyl with the vanadium compound. The amount of the diisopropyl ether used to prepare the addition compound can vary within wide limits. For instance, the addition compound can be formed from equimolar amounts of the aluminium alkyl and the diisopropyl ether but it is preferread to employ an excess of the diisopropyl ether. An amount of diisopropyl ether of up to 4 moles per mole of aluminium alkyl can advantageously be employed. Preferably, about 3 moles of diisopropyl ether are employed per mole of aluminium alkyl.

The preferred catalyst consists of a mixture of a vanadium halide and an addition compound of an aluminium alkyl and diisopropyl ether. The preferred halides of vanadium are the chlorides, for example vanadium trichloride and the oxychlorides. Mixtures of vanadium trichloride and vanadium oxytrichloride can be used, if desired.

The preferred aluminium alkyls are those having the formula AlR_3 wherein Al represents aluminium, and R represents an alkyl group containing up to 8 carbon atoms, for example isobutyl, ethyl, isopropyl or octyl.

The proportion of the addition compound used is preferably from 0.5 to 3 per cent based on the total weight of the monomer and the surface-active catalyst.

Generally, an amount of up to 10 moles of aluminium alkyl per mole of vanadium compound can be employed, but usually the amount is at least 1.5 moles.

If desired, the surface-active catalyst can be absorbed on cryolite or on another finely-divided filler, for example silica or carbon black. The silica can consist of either a three-dimensional cross-linked network, or a lattice distorted by the presence of an element of

variable valency such as chromium or iron.

The polymerization reaction is usually conducted in a liquid medium which acts as a solvent for the monomer, in the absence of moisture and oxygen. The polymerization is usually conducted at atmospheric pressure but it can be conducted at a higher pressure, if desired. The temperature of polymerization can vary within wide limits and it depends to some extent on the monomers being polymerized and on the catalyst being used to effect the polymerization. For instance, the polymerization can be effected at a temperature between room temperature and about 80°C., say for instance, 50°C.

Various classes of hydrocarbons or their mixtures which are liquid under the polymerization conditions can be used as the liquid reaction medium. The liquid reaction medium should be chemically-inert to the monomer and the surface-active catalyst. The saturated aliphatic hydrocarbons, alkanes, and cycloalkanes are especially suitable as reaction media and include n-pentane, n-hexane, 2,3-dimethylbutane, n-octane, isooctane, 2,2,4-trimethylpentane, cyclohexane, and dimethylcyclopentane. Members of the aromatic hydrocarbon series, particularly the mononuclear aromatic hydrocarbons, e.g. benzene, toluene, xylene, and mesitylene can be employed and, in addition, other compounds such as ethyl-benzene, ethyl-toluene, and isopropyl-benzene.

The ratio by volume of liquid reaction medium to polymer is generally not more than 3:1. Polymers prepared in accordance with the present invention are usually soluble in the liquid reaction medium.

The process of this invention is particularly suitable when applied to polymerizing conjugated diolefines including unsubstituted dienes, e.g. butadiene, and substituted dienes, e.g. isoprene. Other monomers such as propylene, butene-1, and ethylene, can be polymerized or copolymerized.

The use of a surface-active catalyst formed from a vanadium compound and an addition compound of an aluminium alkyl and diisopropyl ether has important advantages. Firstly, a high polymerization rate is obtained when the catalyst is used. The rate is much higher than when other ethers are used. Secondly, the polymer obtained contains a high proportion or a stereo-regulated fraction. The surface-active catalyst can be employed to good effect in industrial polymerization systems and enables an increase in production of high quality polymers to be attained.

The effect of the use of an addition compound of aluminium triethyl and diisopropyl ether is shown in the accompanying drawing. An experiment was carried out similar to that described in Example 3 following, in which the polymerization of isoprene was effected employing, as a catalyst, vanadium trichloride and an addition compound of aluminium triethyl and diisopropyl ether. The molar ratio of the ingredients of the catalyst was 1:2:6 for $VCl_3:Al(C_2H_5)_3$: diisopropyl ether. The percentage conversion at the end of chosen periods was plotted in the form of a graph, and the results, are shown by the line 'A'. An experiment was carried out employing a molar ratio of $VCl_3:Al(C_2H_5)_3$: diisopropyl ether of 1:2:2, and the results are shown by the line 'B' on the graph. A further experiment was carried out in which the diisopropyl ether was omitted from the catalyst, and the molar ratio of vanadium trichloride: aluminium triethyl was 1:2. The results of this experiment were plotted as line 'C'. It will be seen from the graph that the use of diisopropyl ether and vanadium trichloride greatly increases the rate of polymerization.

The invention is illustrated in the following Examples:—

Example 1

This Example illustrates the polymerization of isoprene.

Finely-divided vanadium trichloride (0.1701 gm) was dispersed in 5 ml SBP. and 0.2975 ml of aluminium triethyl, added with shaking under dry nitrogen. The mixture was allowed to stand overnight at room temperature. 0.305 ml of dry isopropyl-ether was then added to the mixture and shaken thoroughly.

The catalyst mixture was charged under nitrogen into a bottle and diluted with 15 ml of SBP and 10 gm. of isoprene added, and the bottle closed.

The bottle was heated at 50°C. for 1½ hours, being shaken intermittently and at the end of this time, the bottle contained an extremely viscous polymer solution which was just mobile. The polymer solution was allowed to stand overnight for 16 hours at room temperature, at the end of which time the contents had become solid. The polymer was recovered from the solution by the usual techniques, giving a 95 per cent yield.

S.B.P. is a commercial aliphatic hydrocarbon solvent consistink primarily of hexane.

Example 2

The procedure described in Example 1 was repeated but the catalyst was prepared from a mixture containing 0.0939 gm. of vanadium trichloride and 0.1642 ml of aluminium triethyl. After standing for 16 hours, 0.1685 ml of di-isopropyl ether and 10 gm of isoprene were added, and the solvent to monomer ratio increased to 5 to 1.

The mixture so obtained was heated at 50°C. for 3 hours with occasional shaking, and then left to stand at room temperature for 16 hours.

The polyisoprene was recovered from the mixture in 80% yield.

EXAMPLE 3

The procedure described in Example 1 was repeated but using a Sutherland reactor charged with a dispersion of 2.6817 gm. of the vanadium trichloride in 100 ml or SBP 62/68. 3.76 gm. of aluminium triethyl were added and the whole allowed to mature overnight. 4.82 gm. of di-isopropyl ether were added, followed by 1150 ml SBP 62/68 and 170 gm. of isoprene. After stirring the mixture for approximately 1 minute, the contents of the reactor were allowed to stand for 16 hours at 50°C. and 48 hours at 20°C.

The polyisoprene was recovered from the reaction mixture in a 58 per cent yield.

EXAMPLE 4

A dispersion of 2.5 gm. of the vanadium trichloride in a solution of 3.5 gm. of aluminium triethyl in 10 ml. of SBP 62/68 were allowed to react in a funnel under nitrogen for 16 hours. 4.48 ml. of diisopropyl ether were then added under nitrogen and the whole catalyst mixture vigorously shaken.

This catalyst was transferred under nitrogen to a Sutherland reactor and 200 mls of isoprene added. The reactor charge was stirred continuously for 19 hours at 50°C.

The polyisoprene was recovered from the reaction mixture in a 59 per cent yield.

EXAMPLES 5—9

The effect of the incorporation of an ether in the catalyst mixture is clearly chown in the following Table I, which contains the essential features of Examples 1 to 4 and in addition details of other experiments carried out with and without the presence of an ether.

TABLE I

Example	Solvent/ Monomer	Catalyst concentration (Total on monomer)	Ether	Time (hr)	Temp. (°C.)	Yield (%)
1	1.4	4.76	Yes	1.5 16	50 20	95
2	5	2.58	Yes	3 16	50 20	80
3	5	3.76	Yes	16 48	50 20	58
4	5	4.4	Yes	19	50	59
5	10	4.5	Yes	68	50	57.5
6	3*	4.5	Yes	24	50	58
7	5	3	No	40	50	48
8	5	5.5	No	44	50	32
9	5	4.5	No	43	50	26

* Initially, increasing to 9 during the reaction.

It can be seen that the use of an ether increases the yield obtainable and allows a shorter reaction time to be employed.

EXAMPLES 10

This Example illustrates the advantage of the use of diisopropyl ether in the formation of an addition compound when compared with various other ethers.

Five experiments were carried out employing a technique similar to that used in Example 3, in which isoprene was polymerized with aluminium triethyl and vanadium trichloride. The aluminium triethyl was complexed with one of the various ethers listed in Table 2. Polymerizations were carried out for 16 hours at 50°C.. Other details as to the amount of monomer and solvent, and catalyst constituents are shown in Table 2.

TABLE 2

	Experiment No.				
	1	2	3	4	5
Isoprene	100 ml	100	100	100	100
Petrol	500 ml	500	500	500	500
Aluminium triethyl	1.07 gm	1.07	1.07	1.07	.107
Vanadium trichloride	1.08 gm	1.08	1.08	1.08	1.08
Diisopropyl ether	1.92 ml	—	—	—	—
Diethyl ether	—	1.66 ml	—	—	—
Dichlorodiethyl ether	—	—	1.58 ml	—	—
Anisole	—	—	—	1.25 ml	—
Time, 16 hrs @ 50°C. Conversion to *trans*-1:4-polyisoprene	75%	4%	1%	5%	less than 1%

It will be seen from the above Table 2 that the use of diisopropyl ether enables a high degree of conversion to the trans-1:4-polyisoprene to be obtained. This is not the case with the other ethers.

WHAT WE CLAIM IS:—

1. A process for the polymerization of an unsaturated aliphatic compound containing a $CH_2{=}\overset{|}{C}$— group which comprises forming a heterogeneous surface-active catalyst by mixing together a vanadium compound with an addition compound of an aluminium alkyl with diisopropyl ether, and contacting the aliphatic compound with said catalyst.

2. A process according to claim 1 wherein the catalyst is prepared by mixing the aluminium alkyl with diisopropyl ether prior to the addition of the vanadium compound.

3. A process accordong to claim 1 wherein the catalyst is prepared by mixing the aluminium alkyl and the vanadium compound, and adding diisopropyl ether to the mixture.

4. A process according to any one of the preceding claims wherein up to 4 moles of diisopropyl ether are employed per mole of aluminium alkyl to effect the formation of an addition compound.

5. A process according to claim 4 wherein 3 moles of diiropropyl ether are employed per mole of aluminium alkyl to effect the formation of the addition compound.

6. A process according to any one of the preceding claims wherein up to 10 moles of aluminium alkyl per mole of vanadium compound are employed to produce the heterogeneous surface-active catalyst.

7. A process according to claim 6 wherein at least 1.5 moles of aluminium alkyl per mole of vanadium compound are employed to effect the formation of the heterogeneous surface-active catalyst.

8. A process according to any one of the preceding claims wherein the amount of the addition compound of aluminium alkyl and the diisopropyl ether is from 0.5 to 3 per cent by weight fo the total weight of the monomer of the surface-active catalyst.

9. A process according to any one of the preceding claims wherein the vanadium compound is a vanadium halide.

10. A process according to claim 9 wherein the vanadium halide is vanadium trichloride.

11. A process according to any one of claims 1 to 8 wherein the vanadium compound is a vanadium oxyhalide.

12. A process according to claim 11 wherein the vanadium oxyhalide is vanadium oxytrichloride.

13. A process according to any one of the preceding claims wherein the aluminium alkyl has the formula AlR_3 wherein R represents an alkyl group containing up to 8 carbon atoms.

14. A process according to claim 13 wherein the aluminium alkyl is aluminium triethyl.

15. A process according to any one of the preceding claims wherein the surface-active catalyst is absorbed on a finely-divided filler material.

16. A process according to any one of the

preceding claims wherein the monomer is dissolved in an organic hydrocarbon compound that is chemically-inert to the monomer and to the surface-active catalyst.

17. A process according to any one of the preceding claims wherein the unsaturated aliphatic compound is isoprene.

18. A process for the polymerization of an unsaturated aliphatic compound according to claim 1 substantially as described in the foregoing Examples.

19. A polymer of an unsaturated aliphatic compound when prepared by the process of any one of the preceding claims.

C. H. BOWLER,
Agent for the Applicants.

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1015054 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale